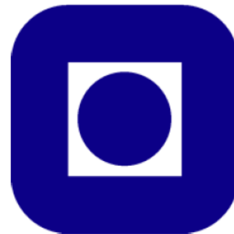
NORWEGIAN UNIVERSITY OF SCIENCE AND TECHNOLOGY



ST7: Membrane Ultrafiltration 2021

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1 Introduction

All filtration methods aim to attain the separation of substances. Ultrafiltration is not fundamentally different from microfiltration, nanofiltration or gas separation, except in terms of the size of the molecules it retains (10^{-3}–10^{-6}Da).

Typically, ultrafiltration membranes will remove high molecular-weight substances, colloidal materials, and organic and inorganic polymeric molecules, while low molecular-weight organics and ions are not removed. Because only high-molecular weight species are removed, ultrafiltration achieves high flux rates at low applied pressure. This makes ultrafiltration the ideal filtration method to introduce the basic principles of filtration such as flux, permeability and rejection, which this experiment aims at.

2 Theory

Membranes are surfaces with partially transmitting structures, which are at least permeable to one of the components of the surrounding fluid and impenetrable to the other components [1]. Figure 1 illustrates the process of a semi-permeable barrier: one component (permeate) of the mixture to be separated (feed) passes through such barrier easier than the other. In general, the rate at which a particular component moves through the membrane is determined by the size of the molecule, the concentration, the pressure difference across the membrane and the affinity of the component for the membrane material. Ultrafiltration membranes are porous with a typical pore diameter in the range of 10 to 100 nm.

However, it is more customary to categorize membranes by molecular-weight cut-off (MWCO), which is defined as a molecular size of dextran being 90% rejected by the membrane. For instance, a membrane that removes dissolved solids with molecular weights of 10 kDa and higher has a MWCO of 10 kDa. Obviously, different membranes even with the same molecular-weight cut-off will have different pore size distribution. In other words, different membranes may remove species of different molecular weights to different extent. Nevertheless, molecular-weight cut-off serves as a useful guide when selecting a membrane for a particular application [2].

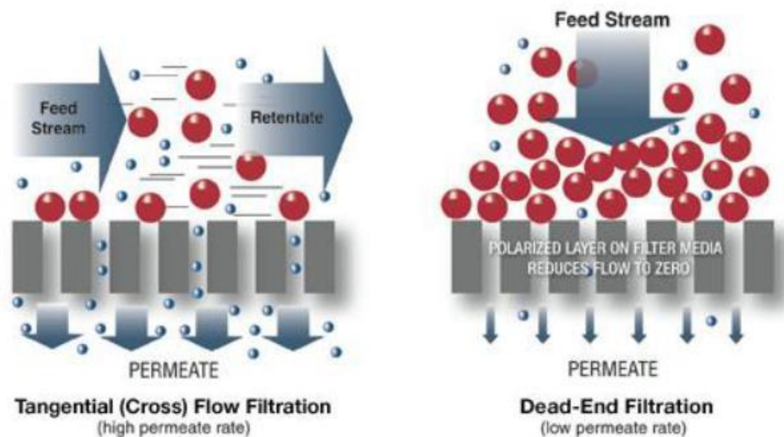

Figure 1: Schematic illustration of membrane separation.

Pressure-driven membrane processes are increasingly being incorporated in industrial plants to separate valuable chemical and biological compounds from mixtures. Ultrafiltration processes (UF) in particularly have become increasingly important during the past decades due to their mild and energetically favorable separation and concentration technique, which have been commercialized in pharmaceutical, chemical, and food industries. Among the main problems of ultrafiltration are concentration polarization and fouling because both phenomena give rise to flux decline. The flux decrease may also be due to an increase in osmotic pressure, formation of gel layer, solute adsorption on the membrane, and pore plugging.

The flux decline also depends on the flow direction and operating condition. Two different arrangements are common in filtration:

i) The dead-end filtration, where the feed flow is directed perpendicular to the membrane.

ii) The cross-flow filtration, where the feed flow is directed parallel or tangential to the membrane.

The former one is most often used for small volume laboratory applications and the latter one is used for large volume process applications [3, 4]. When a membrane is used for separation, the concentration of any species being removed is higher near the membrane surface than it is in the bulk of the stream. This condition is known as concentration polarization and exists in all ultrafiltration and reverse osmosis separations. The result of concentration polarization is the formation of a boundary layer. The thickness of the layer and its concentration depends on the mass of transfer conditions that exist in the membrane system.

Membrane flux and feed flow velocity are both important in controlling the thickness and the concentration in the boundary layer. The boundary layer impedes the flow of water through the membrane. The high concentration of species in the boundary layer produces permeate of inferior quality; therefore are in ultrafiltration applications relatively high fluid velocities along the membrane surface maintained to reduce the concentration polarization effect [2].

One of the most critical parameters in the characterization of membranes is the flux $\boldsymbol{J}$. For the characterization of clean membranes flux is measured with deionized water as "pure water flux". The definition of the instantaneous flux (Equation 1) is given by:

$$J_v = \frac{1}{A} * \frac{\Delta V}{\Delta t}\left[\frac{m^3}{m^2 s}\right] \tag{1}$$

Where "$\boldsymbol{V}$" is the filtration volume, "$\boldsymbol{t}$" the filtration time, and "$\boldsymbol{A}$" the membrane surface area. Also of interest in an ultrafiltration process is the permeability $\boldsymbol{L_p}$ (Equation 2) with respect to the solvent:

$$L_p = \frac{J_v}{\Delta P}\left[\frac{m}{bar * s}\right] \tag{2}$$

Where $\boldsymbol{J_v}$ is the volumetric filtration flux (volume flow rate per unit membrane area) and $\boldsymbol{\Delta P}$ is the transmembrane pressure driving force. $\boldsymbol{L_p}$ is often referred to as the hydrodynamic permeability since water is the typical solvent, and the data are often normalized by the solvent viscosity to account for the effects of temperature [5].

In its most basic form, ultrafiltration is a pressure-driven process designed to remove solvent (typically water) and small solutes (e.g., salts and sugars) from larger macromolecules (e.g., proteins). Mass transport is dominated by convection; the rate of mass transport for both the product and the small impurities is proportional to the filtration flux and the corresponding solute sieving coefficients ($\boldsymbol{S_i}$), where $\boldsymbol{S_i}$ is equal to the ratio of the solute concentration in the filtrate to that in the bulk (feed) solution. The sieving coefficient is simply equal to $\boldsymbol{1-R}$ where $\boldsymbol{R}$ is the rejection coefficient (Equation 3) [5].

$$S_i = \frac{C_{pi}}{C_{fi}} = 1 - R \rightarrow R = 1 - \frac{C_{pi}}{C_{fi}} \quad (3)$$

This definition is the apparent rejection calculated from the feed concentration $\boldsymbol{C_f}$ and the permeate concentration $\boldsymbol{C_p}$, for component i. The true membrane rejection is higher due to concentration changes in the boundary layer. However, the values of the concentration in the boundary layer are not accessible [6].

3 Experiment

3.1 Experimental Setup

All filtration experiments are to be done in a Stirred Ultrafiltration Cell Model 8400 from Millipore. The membranes are circular flat sheets with a diameter of 76 mm (Filtration Area: 41.8 cm^2). The test cell is schematically illustrated in the figure below. Figure 2 is operated in the dead-end filtration mode with feed side being pressurized.

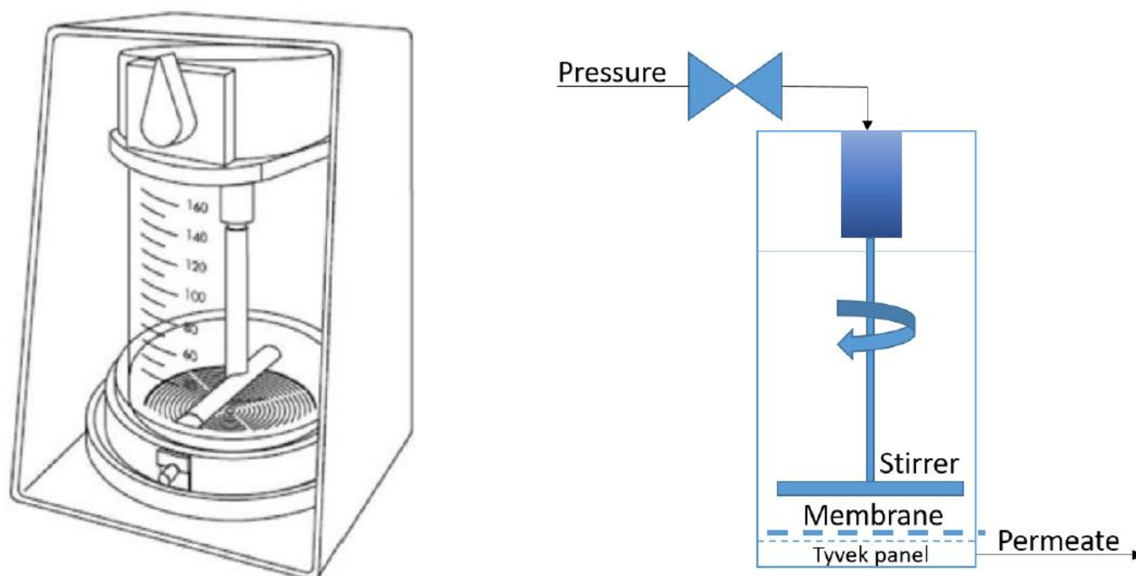

Figure 2: The Stirred Ultrafiltration Cell Model 8400 and its setup scheme.

The filtration cell has a volume of 400 ml and the transmembrane-pressure is controlled by a pressure gauge. The stirrer speed is controlled by a magnetic stirrer underneath the cell. The permeate mass is measured over time with a laboratory scale and monitored with the Labview software (connected computer).

3.2 Cell assembly

The different parts of the ultrafiltration cell are presented in Figure 3.

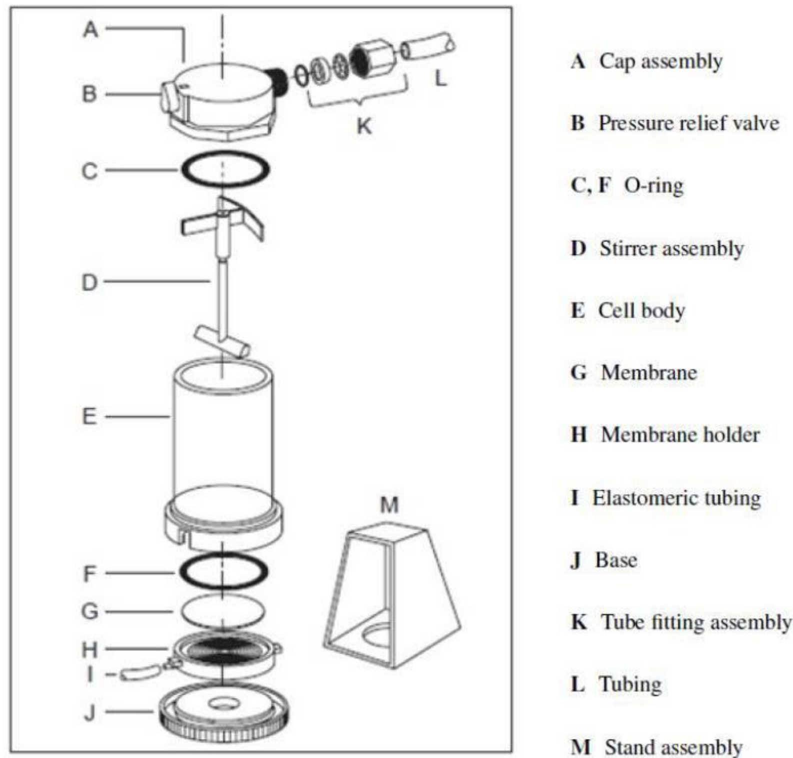

Figure 3: Overview of the different parts in the ultrafiltration cell.

When handling the membrane (G) it is important to avoid contaminating or scratching it, so wear gloves or be careful to hold the membrane by its edges. First place the membrane into the membrane holder (H)making sure the shiny side is facing upwards (remove blue protection). Place the O-ring (F) on top of the membrane and push it down gently to fit the membrane evenly in the bottom of the holder. Place the membrane holder on the bottom of the cell body (E) and fit the base (J) over the holder. Screw the base firmly to the body to avoid air leakage when the cell is pressurized. Check that the filtrate exit tubing (I) fits firmly onto the exit spout of the membrane holder.

Place the stirrer assembly (D) into the cell body and pour the given feed into the cell. Take the cap assembly (A, the O-ring (C) should already be in place) and push it down onto the cell body. In this step it is necessary to use some force and at the same time make a twisting motion. If there is difficulty fitting the cap assembly on the cell, lightly lubricate the O-ring, while making sure no gel gets

on the inside of the cell. Make sure the pressure relief valve (B) is oriented in the same direction as the filtrate exit port (should be on the same side of the cell).

Place the cell body into the stand assembly (M) and turn the pressure relief valve to the closed (vertical) position. Fit the tubing of the gas pressure line (L) to the cap assembly and tighten the hexagonal nut (K). Place a beaker on the laboratory scale next to the ultrafiltration cell so that the tubing on the exit spout of the membrane holder is directed into the beaker without touching it.

3.3 Experimental procedure

Only one membrane should be used throughout the experiment. The membrane need to be rinsed with deionized water in order to wash out the conservation agents from the pores. The transmembrane pressure should be set to 1bar, or an alternative pressure given by the supervisor. Pressure should be kept constant, this may be difficult, but be sure to check the pressure during your experiment and adjust accordingly. The pressure should be kept around 1 bar (0.9-1.1 bar, as long as you keep it constant and use the applied pressure in your calculations). During filtration, the stirrer should not overcome 100 rpm. The feed volume should be around 100 ml.

How to use the balance and Labview software (measures change in mass as a function of time.):

a. Tare the balance.

b. Start Labview.

c. Make a test file to ensure connection between balance and computer.

d. If no connection, restart software and make a new test file.

Conductivity and temperature are measured by the conductivity meter.

4 Experimental tasks

4.1 Pure Water Permeability

Start the experiment by filtrating deionized water to find pure water flux and permeability for the membrane. Repeat the filtration with another batch of deionized water to establish a possible change of the membrane performance. Repeat this part until similar results are achieved (2-3 rounds, about 2 min for each round). Make separate files in labview for each filtration.

Note for all filtrations: temperature and conductivity before and after filtration.

4.2 Unknown sample filtration

Do a finale filtration with a sample of unknown concentration, provided by the supervisor. Calculate flux and permeability of the provided sample. Again, do not forget to note the temperature and conductivity of the sample before and after filtration.

4.3 Calibration curve

Prepare different solutions of known concentration (1-25 g/l) and determine their conductivity (note temperature), while filtrating the unknown concentration sample. In the end, determine the concentration of feed and permeate of unknown sample based on the calibration curve.

4.4 Compare results

If possible, please collect permeability and flux values from other (min. 2) groups to compare results and include as a part of the discussion in your report.

5 Work Plan

Follow the work plan guidelines. In the work plan, a hypothesis (couple of sentences) should be included to describe what you expect to learn/observe from the experiment based on theory. This should be further discussed in your report if your hypothesis was correct or not.

Include tables for all values that you should collect during your experiments.

Hand in to supervisor (junbo.yu@ntnu.no) 72 hours before experiment (at latest!).

6 Report

6.1 Theory

• Follow guidelines.

• Should include a theoretical view of all perspectives in the experiment.

• Include enough theory to be able to discuss your results.

6.2 Results

• Present results as you feel benefit your report. All data from your experiment should beincluded in some form (graphs/tables etc.) in the full report (includes Appendix).

• Example of calculations.

6.3 Calculations

• Flux and permeability for both water and unknown concentration samples (through put delta V/delta t, use regression + assume density of water).

• Concentration of unknown sample (before and after filtration).

• Sieving coefficient ***S*** for unknown sample (relate to ***R***).

6.4 Discussion

• Discuss hypothesis written in work plan.

• Link theory and results.

• Reliability of results.

• Comparison of results from other groups.

• Source of error.

7 References

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